IN-SITU TEMPERATURE PROGRAMMED OXIDATION AND REDUCTION OF PdCu NANOPARTICLES FOR FUEL CELL APPLICATIONS

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INTRODUCTION

Polymer electrolyte fuel cells (PEFCs) are the leading contender for automotive hydrogen fuel cells. Economists and scientists are concerned over available Pt resources for the electrocatalysts with future mass-market production. Several methodologies have been adopted to reduce or replace expensive Pt, including the use of other platinum group metals (PGM), i.e. Pd,[1] which is marginally more abundant than Pt and relatively stable in the acidic fuel cell environment compared to non-PGM metals. Building on this rationale, we have attempted to reduce the loading of PGM further by fabricating bimetallic particles consisting of a Pd shell with a predominantly base metal core. The core is inexpensive, protected from the acidic environment by the PGM shell, and yet can still influence the electronic nature of the PGM, such that a more 'Pt-like' valence band structure can be attained. In particular, we have successfully prepared monolayer-capped binary Pd-Cu nanoparticles using organic capping agents to limit particle growth and broadening of the particle size distribution. The subsequent removal of the capping agent is a key step to activate the nanoparticle as an electrocatalyst. Using temperature programmed oxidation (TPO) and reduction (TPR) in combination with either X-ray absorption fine spectra (XAFS) or mass spectrometry (MS) we have examined removal of the capping agent toward improving our understanding of future electrocatalyst design.

EXPERIMENTAL

Synthesis of PdCu nanoparticles for TPO/TPR was from Pd(II) acetate, and Cu(II) acetate, both reduced at elevated temperatures as solutes in 2-ethoxyethanol. A mixture of oleylamine and oleic acid was also dissolved in the solution and used as a capping agent. The composition of the Pd_xCu_y nanoparticles was controlled via the metal precursor ratio. The product was isolated by centrifugation. Catalysts were supported on XC-72R carbon by sonication in hexane and then stirred overnight before being collected and dried under N_2. Typically the Pd_xCu_y/C particles were heated at 300 – 500 °C to remove the capping agent. **XAFS**. Pd K-edge X-ray data were taken at APS Sector 20BM in transmission geometry and calibrated against a standard Pd foil. Data were analyzed using the Athena software[2] based on the Feff code. TPO/TPR was measured using a custom gas chamber with temperature control achieved by a modified furnace surrounding the gas chamber and equipped with a programmable temperature ramp. Samples were pressed with a further aliquot of carbon (XC-72) in a ~ 1:1 ratio to yield a plug 0.4 cm long. **TPO-MS** was performed on a Zeton Altamira instrument. A 10 mg sample was loaded into a quartz tube in the furnace. The reactor was purged with reactor gas and then the temperature increased to 600 °C at a rate of 10 °C min^{-1}. Mass spectroscopy was employed to detect the reaction products.

RESULTS

TPO-XAFS was conducted for Pd/C (Fig. 1), and 1:1 and 1:3 PdCu/C nanoparticles.

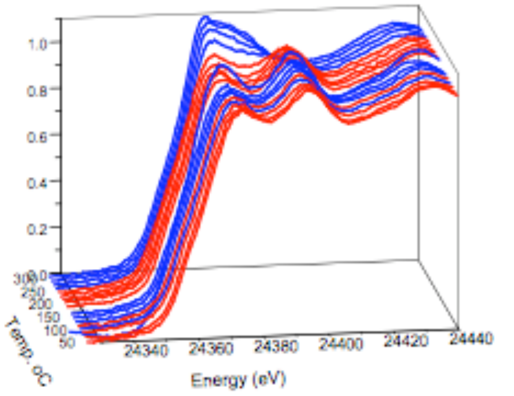

Fig. 1. TPO for Pd/C.

At ~200 °C the capping agents are removed. This is accompanied by severe oxidation of the metal components, such that the lattice structures (A1 *fcc* for Pd/C and PdCu/C, and $L1_2$ cubic for $PdCu_3$) are lost and Pd-O is observed (Fig.2). Cu is oxidized preferentially over Pd, as anticipated from electronic potentials. These findings are supported by TPO-MS.

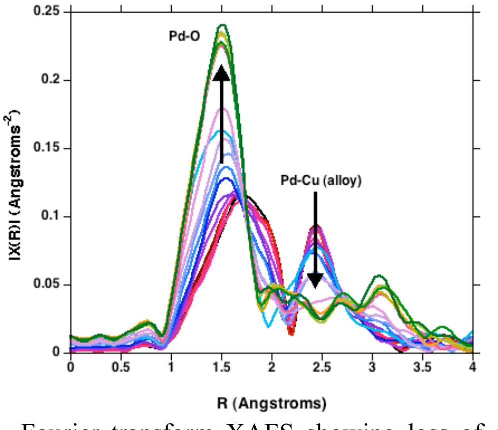

Fig. 2. Fourier transform XAFS showing loss of alloy and formation of oxide with increasing temperature.

Post removal of the capping agent, the Pd/C structure can be regained by reduction in H_2. TPR of PdCu/C catalysts leads to the formation of new phases. We will discuss the XAFS, and metal oxidation and reduction, in terms of lattice structure and future catalyst design.

REFERENCES

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